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A DIRECT ETHANOL FUEL CELL OPERATING AT INTERMEDIATE TEMPERATURE (100-200^{O}C)

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Abstract

Even though investigations regarding DEFC have existed for a few years, there remain problems in terms of efficiency and ethanol crossover. It is considered that the electro-oxidation reaction of ethanol must be complete, involving the release of 12 electrons per ethanol molecule and the breaking of C-C bonds for recovering the maximum energy, that is, it must lead to CO_2. The increasing reaction temperature can enhance the cell performance because thermal activation of electro-chemical reaction is pronounced and operating at higher temperature reduces the adsorbed CO species. The obstacle to increasing temperature is the limitation of the most commonly used Nafion® membrane. The dependence on its water content limits the working temperature (< 100 ^{o}C). Commercial PBI and Nafion-silica membranes were sandwiched in between electrodes prepared using commercial catalysts, carbon supported platinum and platinum-tin as cathode and anode catalysts respectively. The MEAs were tested at temperature of 100-200^{o}C in the single cell. Both membranes could work at operating temperature of 100-200^{o}C. However based-PFSA membranes still needed wet condition to reach better performance. On the other hand, performance of single cell using PBI membrane at dry system was quite comparable with that of single cell using Nafion-silica membrane.

Keywords: *composite Nafion® membrane, PBI, DEFC*

1. Introduction

One limitation of the DEFC is the relatively poor kinetic performance of anode electro-catalysts at low temperature (< 100 ^{o}C). The operation of fuel cells at higher temperature can increase the kinetics of ethanol oxidation and reduce adsorption of intermediates on the anode catalyst acting as poisoning materials. However, a typical membrane for DEFC, a perfluorosulphonated membrane of Nafion®, usually dehydrates at high temperature and leads to high ohmic losses and poor performance. Another restriction is that Nafion® suffers from high ethanol permeability due to the solvated protons going through the water filled ion cluster channels (Ren et al., 2000). Such ethanol permeability (crossover) leads to reduced activity of the oxygen reduction reaction. The development of proton conduction membranes with mechanical and chemical stability at high temperature with minimum ethanol crossover is a potential route to produce economical DEFCs.

This work presents the results of characterisation of Golden Energy-SiO_2 (GE-SiO_2) and PBI membranes. Performance in single fuel cell tests was also investigated at temperatures of 100-200 ^{o}C and compared with the use of a commercial membrane (Golden Energy-SiO_2) and PBI.

2. Experimental

- **Water Uptake**

The membrane water uptake was measured in water at room temperature. It was calculated from the difference in weight between wet and dry samples. The wet weight was determined after immersion of the samples in the water at room temperature for 48 hours. Subsequently, the membrane surfaces were wiped with a tissue paper and weighed immediately. To obtain the dry weight, the samples were heated in an oven at 120 ^{o}C for 2 hours.

The water uptake was determined from:

$$WUT = \frac{m_{wet} - m_{dry}}{m_{dry}} \text{ x } 100\%, \qquad (1)$$

Where *WUT*, m_{wet}, and m_{dry} represented water up take by weight (w.%), and weight of wet and dry membranes, respectively.

- **Permeability Measurements**

Ethanol permeability was measured with a two-compartment glass cell. One compartment was filled with 100 cm^3 of 3 mol cm^{-3} ethanol solution and the other was filled with 100 dm^3 of deionised water. The membrane was clamped between two compartments. Solutions in each compartment were stirred continuously during measurement. Ethanol concentration in the receiving compartment was measured as a function of time by measuring the refractive index of a 0.5 cm^3 sample from each compartment. The observed refractive index was compared to the corresponding value of the calibration curve.

- **Conductivity Measurements**

The membrane conductivity was measured using the four probe technique. The cell was equipped with four platinum foils. The distance between foils was 5 mm. The membranes were cut into 4 x 1 cm strips and positioned across four platinum foils. Current was fed to the membranes by two platinum foils. The other two foils were used to measure the potential drop along the membranes. AC impedance was performed in the frequency range between 1 and 20 kHz. The membrane conductivity was then calculated with the following equation:

$$\sigma = \frac{l}{R\,A} \qquad (2)$$

Where σ is the ionic conductivity, *l* is the distance between the electrodes, *R* is the resistance of the membrane, and *A* is the cross-sectional area.

- **Fuel Cell Test**

Single cell tests were performed with a cell made of titanium having a cross-sectional area of 1 x 1 cm gold coated parallel flow field. Mica filled PTFE was used to border the flow field. An isolated platinum wire connected to the edge of the flow fields acted as a current collector and was put under the mica sheet. The cell temperature was controlled by a thermostat and 3 cartridge heaters were inserted into the cell body.

The performance of the single cell was evaluated by measuring current potential (I-E) characteristic of the MEA using an electronic load (Kenwood PEL 151-201) at a fixed temperature. The MEA was fixed between two flow distribution plates and heated to the required temperature. The single cell was fed with distilled water for about 24 hours to humidify the components. Then the anode was fed with ethanol solution and the cathode was oxygenated for overnight before polarization measurements. The temperature of fuel to the cell was controlled in a heating pipe.

3. Result and Discussions

- **Water uptake**

Water uptake is an important characteristic of a membrane as it provides information on the water retention ability of the membrane. Hydration of a membrane affects its conductivity, mechanical stability, and fuel permeability (Jiang et al., 2006 and Saccà et al., 2006). The water uptake properties of prepared membranes and commercial Nafion® 117 and GE-SiO_2 are listed in Table 1. It is shown that composite membranes have higher water uptake (37 w.%) than the Nafion 117 (25 w.%), which specifies the ability to adsorb more water. An increased water uptake by GE-SiO_2 membranes is due to the hygroscopic affinity of silica and its high water-absorption capacity (Kreuer, 1996 and Kim et al., 2009).

Table 1 The water uptake behaviour of Nafion 117 and GE-SiO_2 membranes at room temperature.

Membranes	Water uptake (w. %)
Nafion 117	25.32
GE-SiO_2 commercial	37.70

- **Ethanol and methanol permeability**

The thickness of GE-SiO_2 and PBI were 60 μm and 50 μm, respectively. Permeability of ethanol and methanol through Nafion® 117, GE-SiO_2, and PBI membranes measured at room temperature is shown in Fig. 1. For the GE-SiO_2 membrane, permeability of ethanol and methanol were 0.6 x 10^{-6} and 1.2 x 10^{-6} cm^2 s^{-1} respectively, whilst for the PBI membrane, their values were 2.6 x 10^{-8} and 7.0 x 10^{-8} cm^2 s^{-1} for ethanol and methanol, respectively. These values are in good agreement with reported values for methanol permeability through Nafion® composite membrane (Li et al., 2009 and Li et al., 2006) and for PBI (Pu et al., 2004). As

expected, GE-SiO_2 and PBI membranes allow lower ethanol and methanol permeability than Nafion® 117 with the order PBI<GE-SiO_2<Nafion® 117; although Nafion® 117 (175 μm) is thicker than others. The presence of silica in ion cluster pores acts as a barrier for ethanol and methanol transport; hence, it reduces ethanol and methanol permeability. Pu et al. (2004) suggested that methanol easily forms a hydrogen bond with PBI compared to Nafion®, which blocks methanol transport through the PBI membrane.

Another observation is that ethanol has a lower permeability value through all membranes than methanol. A similar trend of ethanol and methanol permeability through Nafion® 117 was observed by Xue et al. (2007), with values of 1.48 x 10^{-6} and 1.7 x 10^{-6} cm^2 s^{-1} for ethanol and methanol, respectively.

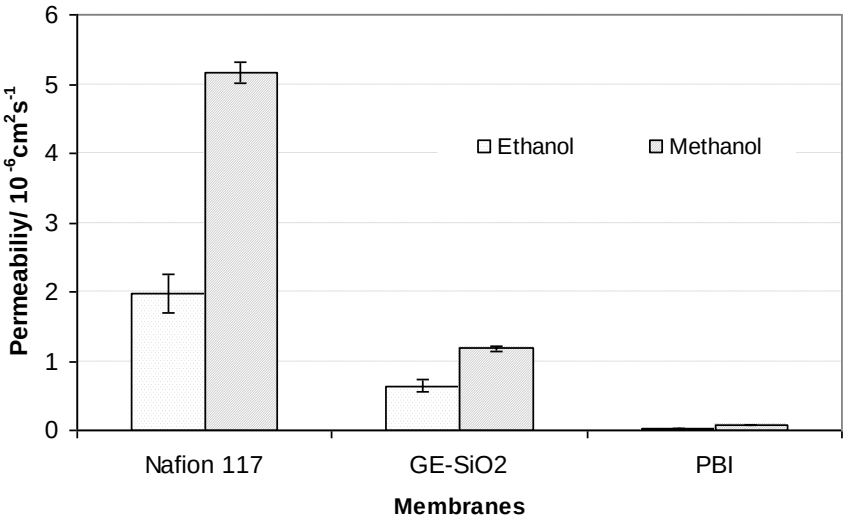

Fig. 1 Permeability of Nafion® 117, commercial GE-SiO2 and PBI membranes at room temperature.

- **Conductivity**

Conductivity of GE-SiO_2 measured at 30 – 110 ^oC under 70 - ~ 100 % relative humidity (RH) is shown in Fig. 2. As temperature increases up to 90 ^oC the proton conductivity of the composite membrane improves progressively from 0.03 to 0.045 S cm^{-1}. These results agree with those reported by the groups of Jiang (2006) and Tominaga (2007). A reduction in conductivity occurred when the temperature increased to 110 ^oC and relative humidity decreased to 70 %. Yuan et al. (2008) also observed a similar trend with Nafion® hollow silica sphere membranes; the conductivity decreased quickly when temperature increased above 100 ^oC. The decrease in conductivity is due to water loss from the membranes through evaporation. The reported conductivity of Nafion® 117 is 0.013 S cm^{-1} (Smitha et al., 2005) under the same condition (lower than that of GE-SiO_2) .This is due to the higher ability of composite membrane to take water up.

The conductivity of the PBI membrane as a function of RH and at temperatures between 120 and 200 ^oC is shown in Fig. 3, as reported by Scott et al. (2007). The conductivity measurement used a 5.6 acid PRU doped. The conductivity of PBI is influenced by temperature, relative humidity, and acid doping level. As shown in Fig. 3, increasing temperature and relative humidity improves conductivity; its values are around 0.02 – 0.06 S cm^{-1}. Similar results were observed by He et al. (2003) using 5.7 acid PRU doped PBI, 0.03-0.08 S cm^{-1} in the range of 110 and 200 ^oC. They also noticed that the conductivity of acid doped PBI depended on the acid doping level (He et al., 2003 and 2006), which was also reported by Bouchet et al. (1999).

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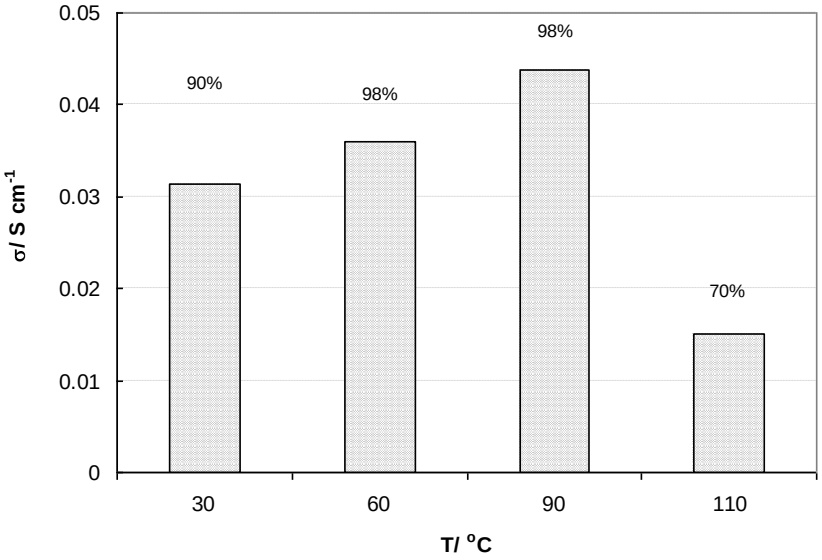

Fig. 2 Conductivity of commercial GE-SiO_2 membrane at varied temperature.

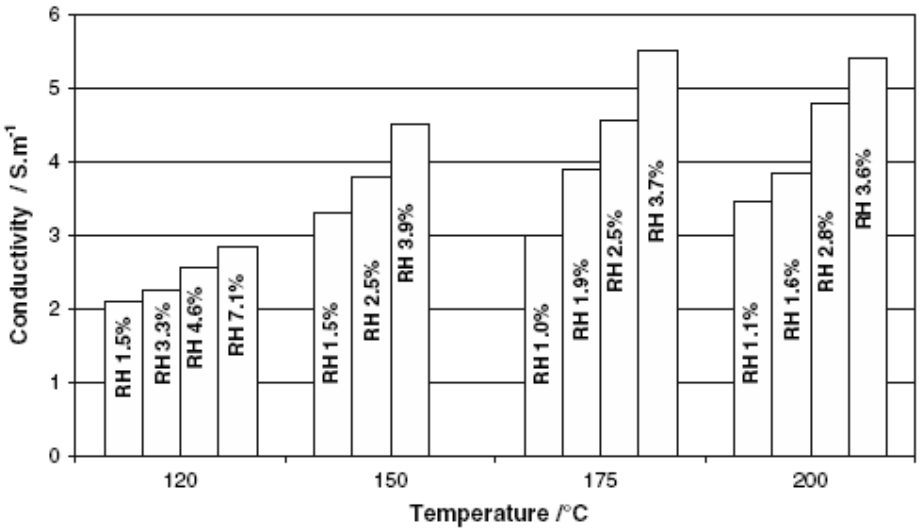

Fig. 3 Conductivity of PBI membrane at varied temperature and relative humidity (Scott et al., 2007).

- **Fuel Cell Test**

A comparison of DEFC performance at an increased working temperature of 110 ^oC is shown in Fig 4. In the ohmic controlled region, polarisation curves of the Nafion® fuel cell showed a higher slope than that of the composite membrane cell. This might have been caused by an increase in the Nafion® membrane resistance due to a lack of humidity, whilst the GE-SiO_2 membrane was able to maintain its water retention at 110 ^oC.

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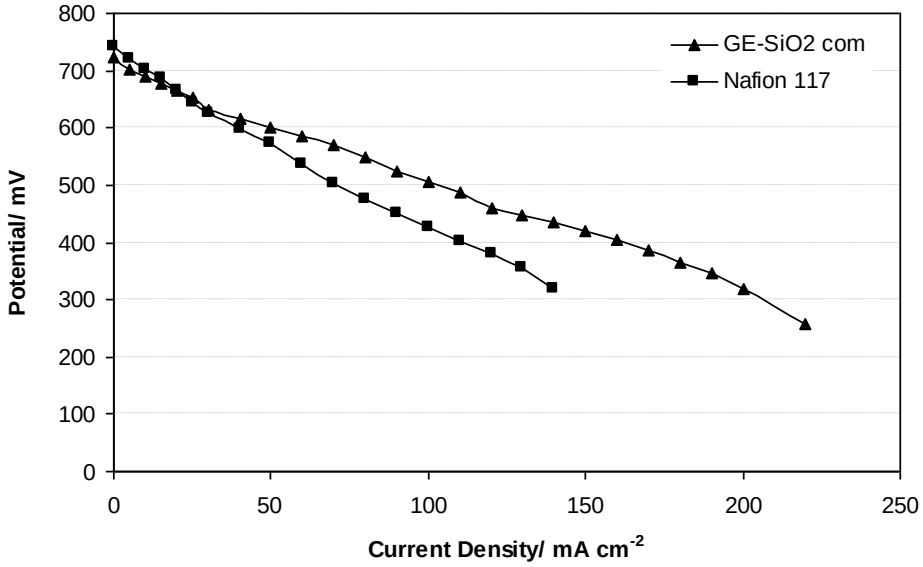

Fig. 4 Polarisation curves of DEFC with commercial Nafion®117 and GE-SiO_2 membrane operated at 110 ^oC and pressures of anode and cathode; 1 and 0.4 barg respectively. Anode: PtSn/C (2 mg Pt cm^{-2}), 2 mol dm^{-3} ethanol. Cathode: Pt/C (1 mg Pt cm^{-2}), unhumidified O_2.

The effect of anode and cathode pressure on polarisation at 110 ^oC is shown in Fig. 5 and Table 2. Increasing pressure at the cathode from ambient pressure to 1 barg considerably improved the OCV from 565 to 754 mV. Although an increase in pressure to 0.4 barg at the anode led to a decrease of OCV from 754 to 723 mV, the power density nearly doubled. This is due to an improvement in behaviour in the ohmic controlled region caused by an increase in conductivity and a reduction in mass transport. A significant power density improvement to 98 mW cm^{-2} occurred when anode pressure increased steadily from 0 to 0.8 barg. It is suggested that an increased anode pressure had a positive influence on the anode kinetics and reduced fuel vaporisation, hence a liquid feed led to maintaining membrane water uptake and reducing mass transport limitation at a high current density, whilst an increased cathode pressure increased cathode kinetics and reduced crossover. Similar results for the polarisation of composite Nafion® DFMC performance were observed by Arico et al. (2003); operating pressure influenced the reaction kinetics, membrane hydration, and mass transport at high current density.

PBI membranes were tested in the single DEFC with a 1 mg Pt cm^{-2} loading of PtSn/C anode catalyst and a 1 mg Pt cm^{-2} loading of Pt/C cathode catalyst. The acid employed on both electrodes was 2 mg cm^{-2}. Performance of cell polarisation with the effect of temperature under conditions of 2 mol dm^{-3} ethanol and oxygen feed without pressuring is presented in Fig. 6.

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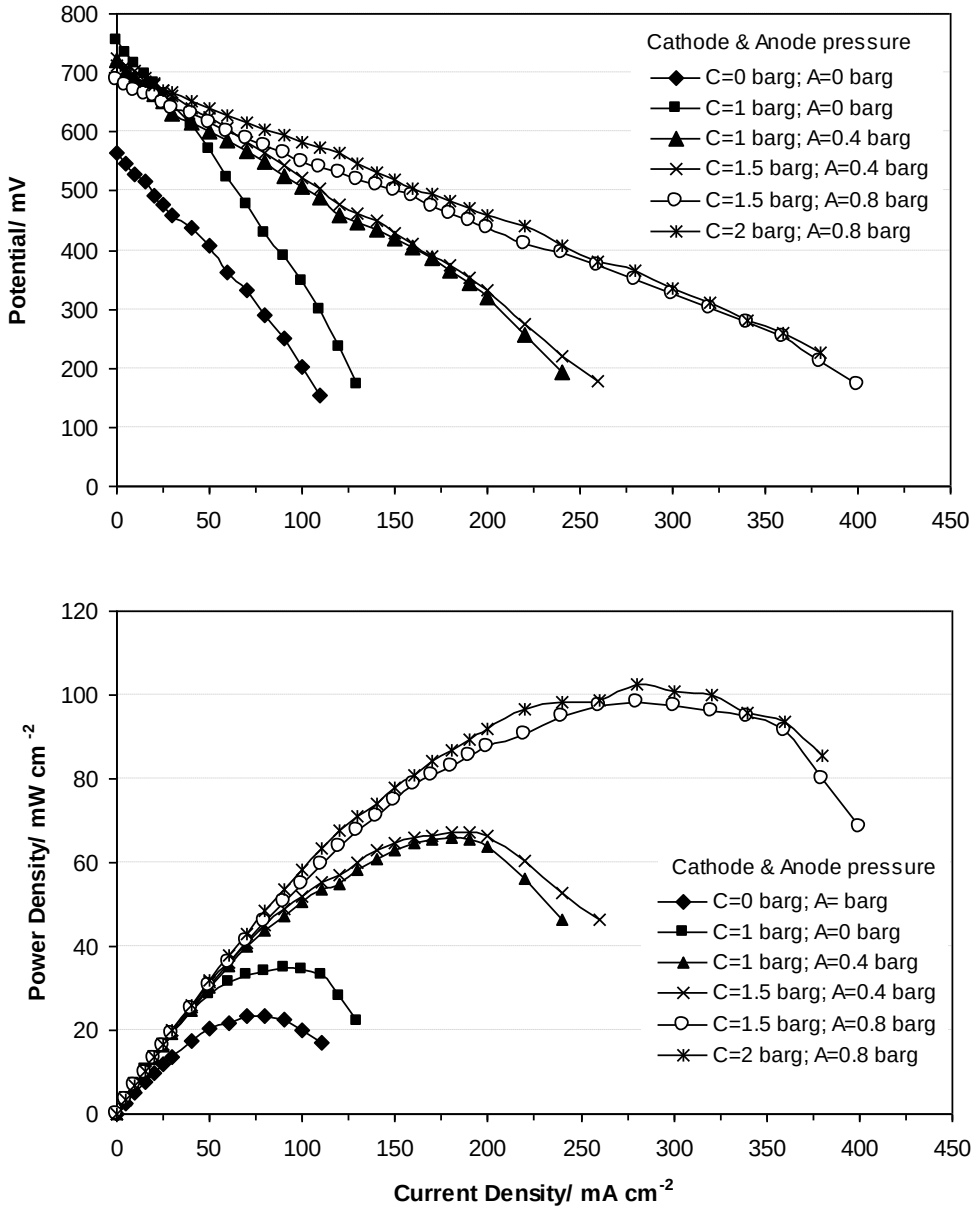

Fig. 5 Polarisation and power density curves of DEFC with commercial GE-SiO_2 membrane operated at 110 ^oC and different pressures of anode and cathode. Anode: PtSn/C (2 mg Pt cm^{-2}), 2 mol dm^{-3} ethanol. Cathode: Pt/C (1 mg Pt cm^{-2}), unhumidified O_2.

Generally, an increase in cell temperature improves cell performance. The OCV and power current density increased as operating temperature increased from 125 to 175 ^oC. OCVs and maximum power densities observed were 554, 651, 713 mV and 13, 21, 28 mW cm^{-2} for 125, 150, and 175 ^oC, respectively. After potential losses due to activation in the kinetic region, however, potential decreased at a similar rate as the current density increased in the ohmic region. Peaks of power density were obtained in a current density range between 80 and 110 mA cm^{-2}. Improved performance with temperature is due to a reduction in membrane resistance and an increase in anode and cathode kinetics (Lobato et al., 2008). Laboto et al. (2009) also noticed that the ethanol crossover through PBI increased with temperature. They observed that peak power densities were 12, 30, 47, and 80 mW cm^{-2} at 125, 150, 175 and 200 □C, respectively, for DEFC using acid doped PBI membrane and ~10 mol dm^{-3} ethanol solution feed. Wang and co-workers (1995) reported DEFC performance at 170 ^oC using acid doped PBI membrane and high loading catalysts (4 mg cm^{-2}). The observed OCV and peak power density were nearly 800 mV and 80 mW cm^{-2}, respectively.

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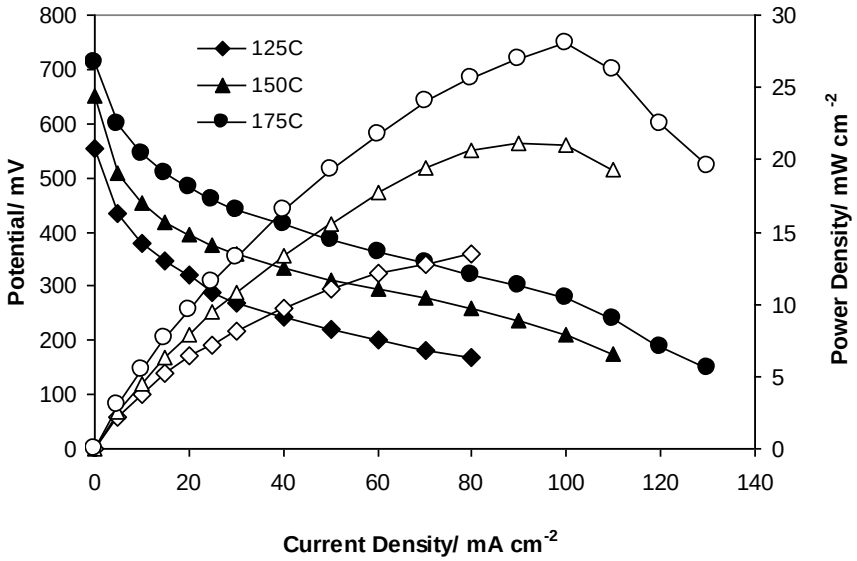

Fig. 6 Polarisation and power density curves of DEFC with PBI membrane operated at different temperature and atmospheric pressure at anode and cathode. Anode: PtSn/C (1 mg Pt cm^{-2}), 2 mol dm^{-3} ethanol. Cathode: Pt/C (1 mg Pt cm^{-2}), unhumidified O_2.

Figure 7 shows polarisation and power density curves with the pressure effect at 175 ^{o}C. An increase in pressure at the cathode improves the OCV and power density. Oxygen reduction is accelerated kinetically with pressure and produces more water. The water produced at the cathode side humidifies the membrane through the back-transport process from the cathode to the anode, thus affecting the ionic conductivity of the membrane Daletou et al., 2009). Penetration of oxygen from the cathode may reduce the crossover effect, and hence the OCV increases.

There was a 15 mV reduction in the OCV, from 775 mV, when the anode pressure increased to 0.4 barg from the atmospheric pressure. Anode pressure led to higher crossover. On the other hand, the partial pressure of ethanol increased with increasing pressure, thus promoting a kinetically anode reaction which caused condensation of the vapour feed; thus, liquid feed affected the membrane conductivity. Less potential losses in the ohmic controlled region may be due to an increase in membrane conductivity.

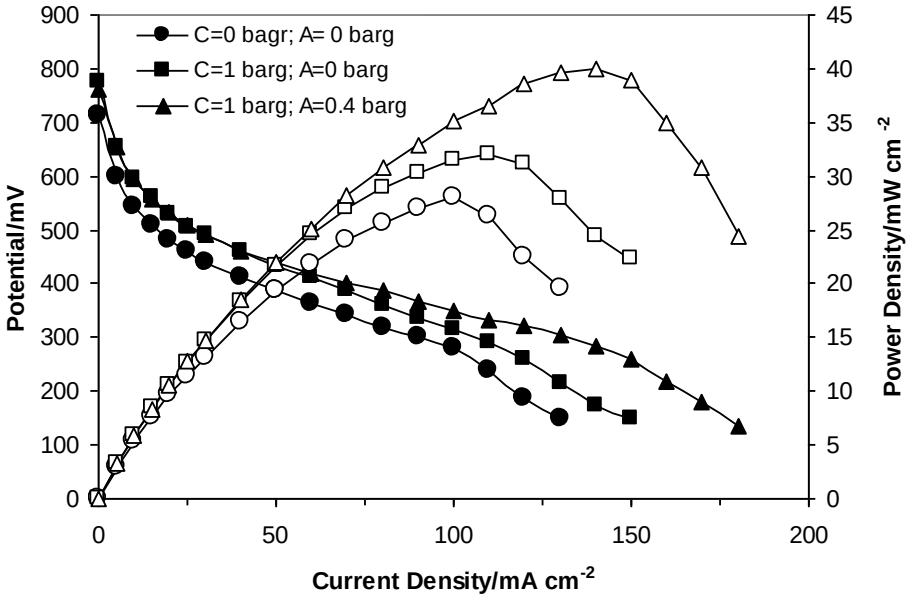

Fig. 7 Polarisation and power density curves of DEFC with PBI membrane operated at 175 ^{o}C and different pressures of anode and cathode. Anode: PtSn/C (1 mg Pt cm^{-2}), 2 mol dm^{-3} ethanol. Cathode: Pt/C (1 mg Pt cm^{-2}), unhumidified O_2.

4. Conclusion

The better performance of DEFC with a composite membrane at a working temperature of 110 ^{o}C was due to higher membrane water uptake, leading to higher proton conductivity. Operation at high anode pressure showed significant improvement. This was due to the increase of liquid fraction in the system, which increased the membrane conductivity.

The PBI-based DEFC operating at 125, 150, and 175 ^{o}C performed with a vapour feed. The temperature and pressure enhanced the cell performance because of improvements in electrode kinetics and PBI conductivity.

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